Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

VII. *On a Series of Combinations derived from Pyroacetic Spirit. By* Robert Kane, M.D., M.R.I.A., *Professor to the Royal Dublin Society and to the Apothecaries Hall of Ireland, Corresponding Member of the Society of Pharmacy and of the Society of Medical Chemistry of Paris, Honorary Member of the Society of Apothecaries of the North of Germany, &c.*

Read 16th March, and 10th April, 1837.

A great deal of labour has been bestowed upon pyroacetic spirit by successive chemists, with but imperfect results towards the development of its real nature. Notwithstanding the researches of Chenevix, Macaire, Mateucchi, and many others, the determination of its composition lately by Liebig and by Dumas, is the only numerical fact belonging to it of which chemists are in possession.

Pyroacetic spirit is known to be generated by heating to redness an acetate of a powerful base, the acetic acid being resolved into carbonic acid and this inflammable liquid; or likewise by passing the vapour of dilute acetic acid through a tube filled with coarse fragments of charcoal, and heated to dull redness. Its composition is found to be per cent.

Carbon = 62.5
Hydrogen = 10.2
Oxygen = 27.3
And its formulæ $C_3 H_3 O$.

The vapour of pyroacetic spirit is found to have a density of 2.022, and the results of the following experiments prove that the atom of pyroacetic spirit corresponds to four volumes of vapour. To represent the combining proportion of this body we must therefore take double the ordinary formula as given above, and consider $C_6 H_6 O_2$ as the constituents of its atom.

It may serve to give a clearer insight into the connexion of the following substances, and to prevent reiteration in the description of them, if a general view of the results be now presented, and the names by which it is proposed to designate these bodies be detailed.

By the loss of successive portions of its oxygen and hydrogen in the form of water, there are obtained from pyroacetic spirit substances having the composition $C_6 H_5 O$ and $C_6 H_4$. By reactions, to be described hereafter, there are produced other bodies having the formulæ $C_6 H_5 Cl$ and $C_6 H_5 I$. The body $C_6 H_5 O$ unites with acids, as the sulphuric and phosphoric, and forms compounds possessing acid properties and forming well characterized salts, the exact composition of which will be hereafter given: in all these reactions it is evident that the pyroacetic spirit follows the same general law as the pyroxylic and the ordinary alcohol; and as there are two theoretical views of the nature of the ordinary ethers, so can two views of the nature of these new bodies be assumed. But whilst I admit the possibility of explaining, perhaps all known phenomena, by each hypothesis, yet as I consider that of common ether, being oxide of ethyl, as most consonant with the general bearing of science, I shall adopt in this paper the corresponding view for the combinations I am about to describe.

The names Acetone and Pyroacetic Spirit, having reference not to the nature, but to one only of the many sources from whence this body can be obtained, it is necessary to substitute for these a name which can be made the foundation of a series, and not indicate any connexion with another substance, which, if real, is at least but accidental. The name Mesit was applied by Reichenbach to a liquid which he met among the products of destructive distillation, and which he took to be pyroacetic spirit; and without at all judging whether that fluid was or was not such, I shall adopt that denomination, and propose for the pyroacetic spirit the name Mesitic Alcohol. We thus obtain

$C_6 H_4$ mesitylene.
$C_6 H_5 O = C_6 H_4 + HO$ mesitic ether; first hydrate of mesitylene.
$C_6 H_5 Cl = C_6 H_4 + HCl$ hydrochlorate of mesitylene.
$C_6 H_5 I = C_6 H_4 + HI$ hydriodate of mesitylene.
$C_6 H_6 O_2 = C_6 H_4 + H_2 O_2$ mesitic alcohol; second hydrate of mesitylene.
$C_6 H_5 O + SO_3$ sulphate of mesitic ether.
$C_6 H_5 O + 2SO_3$ bi-sulphate of mesitic ether.
$C_6 H_5 O + P_2 O_5$ phosphate of mesitic ether.

Or assuming a radical analogous to ethyl, we have, calling it Mesityl,

$C_6 H_5 O$ oxide of mesityl.
$C_6 H_5 Cl$ chloride of mesityl.
$C_6 H_5 O + SO_3$ sulphate of mesityl.
$C_6 H_5 O + HO$ hydrated oxide of mesityl; mesitic alcohol.

I. OF MESITYLENE.

When strong sulphuric acid is mixed with mesitic alcohol, there is immediately very great heat evolved, and the mixture becomes deep brown; if the quantity of acid be considerable, much sulphurous acid gas is evolved. The products of this reaction are complicated, and vary with the proportions of the materials; amongst them are, mesitylene, mesitic ether, and a peculiar solid waxy substance.

To prepare mesitylene, two volumes of pure mesitic alcohol are to be mixed with one of oil of vitriol, and the mixture distilled in a glass retort; by carefully managing the heat there is but very little frothing of the mass until the operation is nearly finished; there comes over a watery liquor, excessively impregnated with sulphurous acid gas, and a yellowish oil, which floats on the surface of it. This amounts in quantity to about one-fourth of the volume of the mesitic alcohol employed. It is to be decanted, and washed very well, to free it from sulphurous acid; then distilled, first in a water-bath, which frees it from a small quantity of the alcohol which had adhered to it, then, the water-bath being removed, the mesitylene distils over pure. The distillation must not be carried too far, as there remains in the retort a quantity of a substance, which, though less volatile, yet contaminates the last distilled portion of the mesitylene. The product is to be digested on well dried chloride of calcium for twenty-four hours, and then poured off, and again distilled. It may thus be obtained pure.

Mesitylene, when pure, is colourless, very light; it boils at about 276° Fahrenheit, and possesses a soft garlic odour, by which it is eminently characterized. It burns with a bright white flame, throwing off much smoke. It is not acted on by alkalies. With sulphuric and nitric acids, and with chlorine, it gives products which will be examined in another part of this memoir.

To determine the composition of mesitylene, the following analyses were made :

I. 0.220 gramme material gave
 0.206 water.
 0.717 carbonic acid.
II. 0.329 material gave
 0.315 water.
 1.054 carbonic acid.
III. 0.248 material gave
 0.236 water.
 0.788 carbonic acid.

These analyses give

	I.	II.	III.
Carbon	= 90.14	88.59	90.08
Hydrogen	= 10.39	10.29	10.55
	100.53	98.88	100.63

The results of these analyses leave no doubt as to the real composition of the substance.

C_6	= 36.78	gives	90.19
H_4	= 4.00		9.81
	40.78		100.00

This body therefore is formed by the abstraction of two atoms of water from the mesitic alcohol, $C_6H_6O_2 - H_2O_2 = C_6H_4$. It occupies in the mesitic series the same position as the olefiant gas in the series of ordinary alcohol.

II. OF MESITIC ETHER.—OXIDE OF MESITYL.

In the reaction of sulphuric acid on the mesitic alcohol this substance is in the first instance produced, but on the heat being raised, the prevailing influence of the sulphuric acid destroys it, taking all the oxygen as water, and reducing the remaining elements to the state of mesitylene. If equal volumes of sulphuric acid and mesitic alcohol be mixed, and the vessel containing them plunged into cold water, to prevent as much as possible the consequent rise of temperature and evolution of sulphurous acid; and, when the deep-brown mixture has become quite cold, it be mixed with twice its volume of water, and allowed to stand for some time; there gradually separates to the surface a thickish fluid, which can be removed by the pipette, and purified by distillation with some lime.

This mass can be separated by rectification into a number of portions of different degrees of volatility. It is mostly mesitylene; it contains likewise a quantity of the solid matter before alluded to, and a quantity of a fluid more volatile than mesitylene, which is mesitic ether. It can be separated by this process only in small quantity, and with difficulty obtained pure; the best way of procuring it is that now to be described.

In the next section will be detailed a process for obtaining an impure chloride of mesityl easily in moderate quantities. This is to be dissolved in alcohol, and to the solution an alcoholic solution of potash added, until the whole becomes strongly alkaline, the liquor being warmed during the operation. There is now to be added six or eight volumes of water; there immediately separates a large quantity of an oily matter coloured yellow, and the liquor contains chloride of potassium. This oil is to be poured on chloride of calcium to dry it; then rectified, to free it from mesitic alcohol which comes over first, and a trace of mesitylene, which is the least volatile of all. This reaction is easily understood: the chlorine passes from the mesityl to the potassium, and the oxygen of the potash takes its place.

Mesitic ether thus obtained, and rendered pure, is limpid, very fluid, and colourless, of an aromatic odour, which may be compared to that of oil of peppermint; it burns with a very luminous, but somewhat smoky flame; it boils at about 248° F. Its combinations with acids will be hereafter described. Its composition was determined by the following analyses:

I. 0,610 gramme material gave
0.582 water.
1.628 carbonic acid.

II. 0.433 material gave

0.410 water.

1.139 carbonic acid.

Giving

	I.	II.
Carbon	= 73.60	72.72
Hydrogen	= 10.59	10.52
Oxygen	= 15.81	16.76
	100.00	100.00

But C_6H_5O gives

C_6	= 36.78	73.88
H_5	= 5.00	10.05
O	= 8.00	16.07
	49.78	100.00

which is evidently its composition.

III. CHLORIDE OF MESITYL.

The preparation of this body in a state of purity proper for analysis is extremely difficult. If liquid muriatic acid and mesitic alcohol be mixed, the mixture assumes a dark colour; but on distillation, the mesitic alcohol is separated almost completely unchanged. If a stream of muriatic acid gas be passed into mesitic alcohol, it is absorbed rapidly and in large quantity, the solution becomes dark-brown, intensely acid and dense. The stream of gas must be continued for several days uninterruptedly, in order to produce the decomposition of two ounces volume of mesitic alcohol. When the dark heavy liquor thus obtained is washed with water, in which it sinks to the bottom, a large quantity of free muriatic acid is given off, and the fluid thus obtained, having been digested on some litharge, and then on fused chloride of calcium, is an impure chloride of mesityl. It sinks rapidly in water; is always dark-coloured; if freshly made it does not affect litmus paper, but being preserved for a night is sufficient to render it so acid as to emit copious muriatic fumes; at the same time it gradually becomes very dark-brown and opaque, and when heated effervesces, owing to the escape of muriatic acid gas. If distilled, a large quantity of muriatic acid gas is set free, and the distilled liquor always floats on water, owing to the quantity of mesitylene and some mesitic ether which it contains. It is consequently impossible to purify this body by rectification.

The substance thus obtained was very often submitted to analysis, but in no case was a satisfactory result obtained. The per cent. composition of a few of the specimens examined is subjoined, in order that the nature of the reaction by which it is generated may be more easily perceived. The determination of the quantity of the chlorine was made in the usual way by passing the vapour of the body over red hot lime.

	I.	II.	III.	
Carbon	= 55.9	64.5	59.9	100.
Hydrogen	= 8.5	9.3	8.6	
Oxygen	= 10.2	12.1	10.5	
Chlorine	= 25.4	14.1	21.0	

On calculating these results, it will at once be seen that the liquids analyzed were mixtures of chloride of mesityl with oxide of mesityl and mesitic alcohol; it is on this account that I made use of this impure substance to prepare the mesitic ether by the action of potash.

By the reaction of perchloride of phosphorus on mesitic alcohol a pure chloride of mesityl can be produced; for this purpose, perchloride of phosphorus is to be added to mesitic alcohol, with which, if not absolutely anhydrous, a lively reaction ensues; water is to be added in successive drops, and the effervescence moderated by placing the vessel in cold water; when a quantity of chloride of phosphorus, about double the weight of the alcohol employed, has been used, three or four volumes of water are to be added; there separates a heavy, slightly-coloured fluid, which is to be washed with the least possible quantity of water, and then poured on some recently fused fragments of chloride of calcium. As it does not dissolve any chloride of calcium, it can be analyzed without distillation, by which process it is in fact in great part destroyed, being resolved into muriatic acid gas and mesitylene. Notwithstanding the care that may be taken in this process, it is difficult to get a product free from mesitic alcohol or ether. In only one analysis did I obtain a result conformable to theory, and consequently that one only need be subjoined.

A. 0.483 gramme material gave

0.294 water.
0.826 carbonic acid.

From whence results

Carbon = 47.27
Hydrogen = 6.67

B. 0.673 material gave 1.252 gramme chloride of silver, corresponding to 45.88 chlorine per cent.

The formula $C_6 H_5 cl$ gives

C_6 =	36.78	47.66
H_5 =	5.0	6.49
cl =	35.42	45.85
	77.20	100.00

It is thus evident that the body analyzed in this instance was chloride of mesityl almost absolutely pure.

IV. IODIDE OF MESITYL.

When iodine, phosphorus, and mesitic alcohol are treated precisely as in the manner for making hydriodic ether by common alcohol, the reaction takes place in the retort without any separation of carbon. Immense quantities of hydriodic acid gas are disengaged, and the liquid which distils over is very heavy, deeply coloured by iodine, and possesses an odour almost exactly similar to that of hydriodic ether. What remains in the retort is slightly tinged yellow, owing to its being mixed with a small quantity of a yellow substance, which is deposited in spangles, like iodide of lead. The liquid remaining in the retort solidifies, on cooling, into a mass of fibrous silky crystals. The distilled liquor, washed with water to remove adhering hydriodic acid, is still coloured by iodine, from which it may be freed by a little water of potash. It very soon again becomes coloured, iodine at first, and then carbon separating, and hydriodic acid gas being given off. This change takes place equally quick, whether the iodide of mesityl be in contact with water or not. In all cases the product is exceedingly impure. I have analyzed very many specimens prepared at different times, and never twice got the same result; there are always present quantities of mesitic alcohol, mesitic ether, and sometimes mesitylene; and as the iodide of mesityl cannot be distilled without undergoing a partial decomposition into mesitylene and hydriodic acid, it has been impossible to effect the purification of the distilled product.

By following a different method of preparation, I have from time to time obtained specimens of this substance, which gave me results approaching closer to the theoretic numbers, than those given by the fluid obtained by distillation. A small quantity of iodine is to be placed in a tube, and about twice its volume of mesitic alcohol to be poured on it; a piece of phosphorus is to be then dropped in; the reaction is to be supported for some time by the application of heat, and then water is to be poured into the tube, and the whole shaken together; a quantity of iodide of mesityl immediately separates, which is purer than any prepared by the process in which the materials are distilled.

The composition given by theory for the iodide of mesityl is,

$$\begin{array}{lrr} \mathrm{C}_6 = & 36.8 & 21.9 \\ \mathrm{H}_5 = & 5.0 & 2.9 \\ \mathrm{I} = & 126.3 & 75.2 \\ \hline & 168.1 & 100.0 \end{array}$$

When chloride of mesityl is distilled with a solution of sulph-hydrate of potassium in alcohol, there is obtained a yellowish fluid, lighter than water, and containing still a large quantity of unaltered chloride, with some mesitic ether; but as it possesses a strong disagreeable smell, and gradually deposits sulphur when kept, I think it very likely that a sulphuret of mesityl can be thus formed. The small quantity I had obtained did not allow me to set about the necessary means of purification.

V. COMBINATIONS OF MESITIC ETHER WITH THE OXYGEN ACIDS.

When mesitic alcohol is mixed with twice its weight of strong oil of vitriol, the mass becomes very hot, dark-brown, and much sulphurous acid gas is formed. When the whole has cooled, it must be diluted with two or three volumes of water, and neutralized by a base; and when the carbonates of baryta, lime, or lead are thus employed, there are formed soluble salts, which have been examined. If the quantity of sulphuric acid employed had been smaller, similar salts are produced; but the substance found combined with the inorganic base is not the bi-sulphate, but the neutral sulphate of mesityl. It appears even that the salts of the proto-sulphate are those most easily formed, as I have sometimes obtained them when I had employed a large quantity of oil of vitriol in order to form bi-sulphate. The sulphate I shall call Sulpho-mesitylic Acid; and the bi-sulphate, Persulpho-mesitylic Acid.

VI. PERSULPHO-MESITYLATE OF LIME.

This salt forms, when evaporated, a deliquescent granular mass, amongst which small prisms are interspersed. It can be completely dried without blackening~~, and~~ thus loses one atom of water of crystallization. When heated strongly it takes fire, blackens, and leaves after ignition a white residue reacting very feebly alkaline. There is no acid whatsoever set free during the decomposition.

A. 0.529 of salt was heated with some nitric acid in a platinum crucible; the decomposition went on very quietly, and there remained a perfectly white residue of sulphate of lime, weighing 0.373, or 70.50 per cent.

B. 0.972 material gave

0.292 water,
0.651 carbonic acid;

or, per cent.

Hydrogen = 3.33
Carbon = 18.52

The formula $2\,SO_3+C_6H_5O+2\,CaO+HO$ gives

$2SO_3$	$= 80.32$	40.95	70.02 sulphate of lime.
$2CaO$	$= 57.04$	29.07	
C_6	$= 36.80$	18.76	
H_6	$= 6.00$	3.06	
O_2	$= 16.02$	8.16	
	196.18	100.00	

This is evidently the true formula.

Persulpho-mesitylate of baryta crystallizes in small pearly plates; when heated it becomes brown, chars, and sulphate of baryta remains; quite neutral.

0.430 salt gave 0.337 of sulphate of baryta, or 78.4 per cent.

The formula $2SO_3 + C_6H_5O + 2BaO + HO$ gives

$2SO_3$	$= 80.3$	27.5	80.0
$2BaO$	$= 153.4$	52.5	
Oxide of mesityl	$= 49.8$	16.7	20.0
Water	$= 9.0$	3.3	
	292.5	100.0	

It was not further analyzed.

The sulpho-mesitylate of lead appeared to be very deliquescent and uncrystallizable; it was not analyzed.

VII. SULPHO-MESITYLATE OF LIME.

This salt is generally formed when the quantity of oil of vitriol, added to the mesitic alcohol, is smaller than to produce the former class of salts; as, when two volumes of the alcohol are mixed with one of vitriol. The solution, when very much concentrated, forms, by cooling, a mass of small crystals not differing much in appearance from the persulpho-mesitylate,—from which, however, the result of analysis at once separates it.

A. 0.625 of this salt in crystals was heated cautiously in a platinum crucible, until all emission of watery vapour had ceased; the salt remained quite white. The residual mass weighed 0.580, or had given 7.2 per cent. of water. These 0.580 were dissolved in water, and decomposed by oxalate of ammonia. The oxalate of lime, collected and burned with the filter, gave 0.244 of carbonate of lime, containing 0.1374 of lime, or 23.7 per cent.

When this salt is warmed with nitric acid, the decomposition is always accompanied with a slight puffing explosion, owing to a very rapid sort of combustion pervading the whole mass. Consequently a quantity of the light residual sulphate of lime is always thrown out of the crucible. The residue is, however, quite neutral, and no free sulphuric acid is given off. In two experiments of this kind the quantities of residual sulphate of lime, although a portion had been lost, were 47 and 53 per cent.

B. 0.765 of the dried salt gave

0.304 water, and
0.848 carbonic acid,

corresponding to

Hydrogen = 4.40
Carbon = 30.29 per cent.

The formula $SO_3 + C_6H_5O + CaO$ gives

SO_3	= 40.16	33.8
CaO	= 28.52	24.1
C_6	= 36.80	31.0
H_5	= 5.00	4.2
O	= 8.00	6.9
	118.48	100.0

The 7.2 of water of crystallization, obtained above, corresponds to one atom; the formula of the crystals therefore is

$$SO_3 + C_6H_5O + CaO + HO.$$

A circumstance in which the salts above described differ from the analogies of the sulpho-vinates, sulpho-mesitylates, and sulpho-napthalates, is that the quantity of the inorganic base is sufficient to neutralize the whole of the sulphuric acid. It is on this account that I have given to the acid first described the name of Persulpho-mesitylic; as the word Bisulpho-mesitylic might imply that the quantity of acid was double that necessary to neutralize the inorganic base present in the salt.

On decomposing the baryta salts of the sulphate or of the bi-sulphate of mesityl, by means of sulphuric acid, some liquors were obtained, which, when heated, began to smell strongly of mesitic ether, and contained free sulphuric acid; evaporated still more, the solutions became black, and sulphurous acid was exhaled. It thus appears that both sulphates are soluble in water, but I was not able to effect their perfect isolation.

It will be at once seen that the salts of the persulpho-mesitylic acid may be represented as double salts, consisting of the sulpho-mesitylate united to sulphate of the same base. Thus

$$2\,SO_3 + C_6\,H_5\,O + 2\,cao + HO$$

is evidently equal to

$$(SO_3 + C_6\,H_5\,O + cao + HO) + cao\,.\,SO_3\,.$$

I will not at present enter into any details connected with this view, which will be at once seen to bear upon the cause of the sulphuric acid retaining its full power of neutralization.

VIII. OF THE HYPO-PHOSPHO-MESITYLOUS ACID.

Of this acid, the existence of which is at present quite without analogy in organic chemistry, only the baryta salt has been examined; the properties and composition of it are, however, so characteristic, as to leave no doubt of its real nature.

When iodide of mesityl is prepared by distilling a mixture of iodine, phosphorus, and mesitic alcohol, there remains in the retort (provided there be some phosphorus in excess) a thick fluid, which, on cooling, solidifies into a mass of crystals resembling amianthus. The decomposition goes on without any separation of carbon; the only products are the iodide of mesityl (impure), the white fibrous crystals, and a very small quantity of a yellow matter, which will be noticed hereafter. These crystals are soluble in water, forming a colourless liquor, with a taste at once strongly acid and intensely bitter. The liquor, neutralized by carbonate of baryta, gives a white insoluble salt, and likewise a soluble one. The solution is to be evaporated nearly to dryness, and then allowed to cool, when it forms a crystalline mass. This mass is then to be boiled in strong alcohol, which dissolves out a quantity of iodide of barium, arising from hydriodic acid with which the crystals had been contaminated in the retort. The boiling in alcohol must be repeated until the residual salt no longer gives any trace of iodine when moistened with nitric acid. It may then be considered pure; as, though prepared at different periods, it has always given the same analytical results. The salt appears as a mass of small white crystalline grains, of an amylaceous appearance, neutral to test paper. When heated it takes fire, burning with a pure phosphorous flame, and throwing off copious fumes of phosphoric acid; when the phosphorus ceases to be emitted the residue is black, but further heated it gives a pure white residue of phosphate of baryta. When moistened with nitric acid, and heated, a very violent reaction ensues, and unless great caution be employed, some of the materials are projected out of the vessel: in any case some phosphorus is lost, being disengaged in the gaseous form. When this salt has been once obtained solid, there is great difficulty in dissolving it completely in water again, although no marked difference of composition can be observed between the portion which dissolves and that which remains unacted on.

0.700 of the salt was moistened with nitric acid, and very cautiously decomposed by heat in a platinum crucible. The action was violent, but without any projection of the solid materials. The residue was treated with nitric acid until it remained white; it weighed 0.520, giving 74.3 per cent. It was dissolved in dilute nitric acid, and the solution precipitated by sulphate of soda. There was obtained 0.467 of sulphate of baryta, corresponding to 43.8 of baryta, from 100 of the salt employed.

0.368 of salt similarly treated gave 0.277 residue; which, dissolved and treated as above, gave 0.247 sulphate of baryta, or 67.1 per cent., containing 44.0 of baryta.

I. 0.469 material gave
0.169 water,
0.346 carbonic acid;

corresponding to

Hydrogen = 4.00
Carbon = 20.40 per cent.

II. 0.566 material gave
0.186 water,
0.399 carbonic acid;

corresponding to

Hydrogen = 3.65
Carbon = 19.49

There are two formulæ by which the properties of this salt can be explained, and with which the analytical results harmonize. One of these assumes the phosphorus to exist half as phosphoric acid and half as phosphuretted hydrogen, the salt containing no water. In the other the phosphorus is represented as being all as hypo-phosphorous acid, while the salt contains an atom of water chemically united, and which cannot be expelled by any temperature not producing complete decomposition. Thus,

$P_2O_5+2BaO+2(C_6H_5O)+P_2H_3$ gives

$2P_2$	= 63.0	17.6
$2BaO$	= 153.4	42.7
C_{12}	= 73.6	20.5
H_{13}	= 13.0	3.6
O_7	= 56.0	15.6
	359.0	100.0

and $P_2O + BaO + C_6H_5O + HO$ gives

P_2	= 31.5	18.0
BaO	= 76.7	43.8
C_6	= 36.8	21.0
H_6	= 6.0	3.5
O_3	= 24.0	13.7
	175.0	100.0

Of these two formulæ, I consider the latter to be much the more probable. We have, even in the inorganic kingdom, but very few examples of phosphuretted hydrogen replacing water, either when the latter is basic or as water of crystallization; and the relation which the oxygen of the two oxides bears to that of the phosphoric acid is not any of those usually met with in the phosphates. On the contrary, the latter formula gives the composition of a basic hypophosphite, which the addition of four atoms of oxygen would change into an ordinary phosphate;

the ratio of the oxygen in the united bases being to that of the acid as three to five.

IX. OF THE PHOSPHO-MESITYLIC ACID.

When glacial phosphoric acid is mixed with its own weight of mesitic alcohol, considerable heat is evolved, and the mixture becomes dark-brown. On neutralizing this liquor with a base, a soluble phospho-mesitylate is obtained, but in very small quantity. The phospho-mesitylate of soda crystallizes in fine rhomboidal plates; exposed to the air the crystals become opaque, owing to the loss of a certain quantity of water by efflorescence. When heated, they melt in their water of crystallization, leaving a white mass; and this, when heated more strongly, froths up, blackens, and finally burns, leaving a white residue of phosphate of soda.

The small quantity of this salt which I had obtained prevented me from analyzing it further than by determining the quantity of water and of phosphate of soda which it contained.

0.379 of the crystallized salt, when warmed cautiously until it ceased to give off watery vapour, but remained quite white, weighed 0.295; and having been then ignited, gave 0.185 phosphate of soda, corresponding to

$$\left.\begin{array}{ll}\text{Water} & =22.2\\ \text{Phosphate of soda} & =48.8\\ \text{Organic matter} & =29.0\end{array}\right\}\ 100.00.$$

The formula $P_2O_5 + C_6H_6O_2 + NaO + 5HO$ gives

$$\left.\begin{array}{ll}\text{Phosphate of soda} & =49.7\\ \text{Mesitic alcohol} & =28.4\\ \text{Water} & =21.9\end{array}\right\}\ 100.00.$$

As an atom of water remained behind with the mesitic ether, it may be considered that he phosphoric acid has three atoms of base and five of water of crystallization. The formula is

$$P_2O_5 + \{NaO + C_6H_5O + HO\} + 5HO.$$

A more detailed examination of these different classes of salts would be a very useful subject for the attention of other chemists.

On the discovery of the compounds which are now about to be described, I was for a time under the impression that I should find, as a product of some of their reactions, the ulmic acid, and consequently I proposed to distinguish the carbo-hydrogen, of which they may be considered to be composed, by the name Pteleyl, from πτελεη, *ulmus;* this radical being also contained in ulmic acid, the formula of which is $5\,(C_6\,H_3\,O_3)$. Now although this acid is not actually formed as a member of the series under examination, yet I am induced to retain the word Pteleyl, as indicating a degree of alliance with it which there is good reason to admit. Provided the name be well understood, the sound does not much signify; and I could not well find a better.

It will be seen that most of the following bodies relate to mesitylene, which indeed bears in this series the place of olefiant gas in that of vinic alcohol; and as the latter may, and indeed should be looked upon as a combination of hydrogen with the radical of acetic acid,—that is, as a hydruret of acetyl,—so may we consider, for the illustration of the following results, the mesitylene as a hydruret of pteleyl,—that is, we make the formula $C_6\,H_4 = C_6\,H_3 + H$.

X. OF THE CHLORIDE OF PTELEYL.

When a current of dry chlorine gas is conducted into pure mesitylene, it is abundantly absorbed with the evolution of much heat and a strong effervescence, owing to the escape of a large quantity of muriatic acid gas. Continuing the supply of chlorine, small needles begin to form at the edge of the fluid, and finally, the whole quantity solidifies into a mass of acicular crystals. These must be dissolved in boiling ether, from which they are deposited in brilliant white four-sided prisms by cooling, whilst the excess of mesitylene remains dissolved; they require to be many times redissolved and recrystallized before they can be considered pure, and must be dried finally by pressure between folds of blotting paper,—not by exposure to the air. These crystals resemble very much those of the commercial di-sulphate of quinine. They are insoluble in water; are not acted on by a solution of potash in alcohol or in water; are volatile without decomposition, but require a high temperature, and can be sublimed in an atmosphere of dry ammonia without alteration. Their composition was determined by the following analyses:

A. 0.352 of the crystals gave

0.145 water,
0.645 carbonic acid;

corresponding to

Carbon = 50.66
Hydrogen = 4.00 per cent.

The difference is necessarily chlorine.

These crystals, added to a new quantity, were recrystallized from ether, and then again analyzed.

B. 0.549 material gave

0.215 water,
0.976 carbonic acid;

corresponding to

$$\left.\begin{array}{ll}\text{Carbon} & = 49.15 \\ \text{Hydrogen} & = \ \ 4.34\end{array}\right\} \ 100.$$

The body consisting of $C_6 H_3 Cl$ gives

$$\left.\begin{array}{ll}\text{Carbon} & = 48.87 \\ \text{Hydrogen} & = \ \ 3.99 \\ \text{Chlorine} & = 47.14\end{array}\right\} \ 100,$$

with which the analyses agree.

The solid substance is thus formed from mesitylene, an atom of hydrogen being replaced by one of chlorine; the hypothetic radical $C_6 H_3$ remaining constant.

XI. OF IODIDE OF PTELEYL.

I have given this name to a substance, of which I have never been able to obtain a quantity sufficient for analysis; but from the circumstances under which it is formed, and the properties I have found it to possess, I believe such to be its nature.

Mesitylene dissolves iodine in large quantity, forming a deep-red solution;

but although exposed to the solar light for several weeks, there is no appearance of alteration. This solution may even be distilled without any change being produced. This mode of reaction, therefore, affords no results.

It has been already mentioned that when iodine, phosphorus, and mesitic alcohol are distilled together, in order to form iodide of mesityl, there is evolved a large quantity of hydriodic acid gas, and much free iodine distils over with the impure iodide of mesityl. In the retort there remains a liquor, which, on cooling, deposits the fibrous crystals of hypophospho-mesitylous acid, with which are mingled small gold-coloured scales, resembling in appearance crystallized iodide of lead. On dissolving the hypophospho-mesitylous acid in water these remain undissolved, and can be separated by the filter; when dried, they lose their brilliant appearance, and form a golden-yellow powder. This powder is insoluble in water, but dissolves in ether, from which it is deposited in brilliant spangles, which again become dull on exposure to the air. It is volatile, but requires a temperature nearly approaching to redness for its volatilization. When cautiously heated, it sublimes without alteration, and forms a brilliant gold-coloured sublimate; but if the vapour be passed through a portion of the tube, previously made very hot, carbon is deposited there, and a large quantity of iodine set free. I attempted to generate this substance by heating together chloride of pteleyl and iodide of lead, but the great part of the chloride sublimed unaltered; and though there were very evident indications of its being produced in minute quantity, the process cannot be employed with advantage.

This substance evidently possesses considerable analogy with iodoforme, (ter-iodide of formyl), which it resembles closely it its appearance, colour, and relation to alcohol, water, and ether. It is, however, completely distinguished from it by its permanence in regard to heat. Dumas states, and I have verified the observation, " A une temperature peu elevée, insuffisante pour charbonner le papier, il se decompose en iode, l'acide hydriodique, et charbon." It is interesting to recollect too, that the formyl is a radical polymeric with pteleyl; the former being C_2H, the latter C_6H_3.

The circumstance of its being formed by the action of iodine on nascent mesitylene, and the great analogy between its properties and those of the chloride of pteleyl, induce me to consider it as the iodide of that radical, and its formula C_6H_3I, giving for its composition

$$\left.\begin{array}{lr}\text{Carbon} & = 22.17\\ \text{Hydrogen} & = 1.75\\ \text{Iodine} & = 76.08\end{array}\right\}\ 100.00.$$

XII. OF HYPO-NITRITE OF OXIDE OF PTELEYL.

When mesitic alcohol is treated with sulphuric acid and peroxide of manganese, it distils over perfectly unaltered if the acid be employed dilute;—and if strong acid be employed, the products are merely mesitylene and traces of mesitic ether;—the manganese being left out of the reaction, and the acid and alcohol acting, as described in the former part of these researches.

If pure mesitic alcohol be mixed with one-half its own volume of strong nitric acid, and the mixture warmed, a very violent effervescence takes place, and a great quantity of red fumes is given off; if the application of the heat be continued for the purpose of distilling the mixture, the decomposition becomes explosively violent, so that on two occasions where it was attempted, the retort was burst. When with the idea of moderating the action a dilute acid is employed, but little change takes place, and the product in the receiver consists of mesitic alcohol quite undecomposed. If, however, on mixing the strong nitric acid and mesitic alcohol, and warming the mixture until the effervescence shall have commenced, the vessel be plunged into cold water, and the action thus retarded,—then again a little warmed, and again cooled, this treatment being repeated several times,—and finally, the whole mixed with five or six volumes of water, there subsides a heavy, pale yellow, fluid, which may be washed with water, until all adhering acid be removed, and then dried by digestion on some fragments of pure chloride of calcium. Thus obtained, this fluid is a mixture of two, and its consistence varies according as the one or the other preponderates, the one being thin, the other about semifluid. The quantity of the latter is greater, according as more red fumes have been driven off; the former predominates when the dilution with water was effected before the decomposition had proceeded far. Neither can be thus obtained absolutely pure, but their nature may be determined with sufficient certainty.

The lighter and thin fluid substance is heavier than water, by which it is gradually decomposed. It is immediately dissolved by an alkali, the liquor becoming dark-brown; and paper dipped in it burning, when dried, with the characters of touch-paper. Its odour and taste are penetrating, but sweetish. When heated in a water-bath, it shows no appearance of vaporization; and if exposed to the flame of a lamp, it is decomposed with an explosion so violent, if a moderately large quantity be employed, as to shatter the apparatus. The products are red fumes of hyponitrous acid, mixed with a very heavy white smoke, and the bottom of the retort is lined with a copious deposit of carbon. These properties completely prevent the purification of the substance by distillation, and render its analysis at once difficult and uncertain in its results. Several experiments were, however, made to determine its composition, which, from the coexistence of the thicker fluid, never gave twice the same absolute result; yet the relation between the quantities of carbon and hydrogen remained in all cases almost constant. Thus the specimen which contained most carbon gave

A. Carbon = 50.43
Hydrogen = 4.35 per cent.

And that which contained least gave

B. Carbon = 44.57
Hydrogen = 4.02

The number of atoms of carbon is to that of hydrogen in A as 6 to 3.17; and in B as 6 to 3.32. It is therefore evident that in both the thin and the thicker fluid the carbon and hydrogen are in very nearly the same ratio as that of $C_6 H_3$. It is also certain that the thin fluid contains nitrogen either as nitric or hyponitrous acid, and we may construct from these principles the formula $C_6 H_3 O_4 N$, which gives

$$\left.\begin{array}{ll} \text{Carbon} & = 42.8 \\ \text{Hydrogen} & = 3.5 \\ \text{Nitrogen} & = 16.5 \\ \text{Oxygen} & = 37.2 \end{array}\right\} 100.$$

The formula $C_6 H_3 NO_4 = C_6 H_3 O + NO_3$; and represents a combination of oxide of pteleyl with hypo-nitrous acid, analogous to the nitrogen compounds existing in the napthaline and other series. The origin of this body may be very simply explained. It is probable that nitric acid unites directly with oxide of mesityl, but produces a compound, which is decomposed by the application of moderate warmth. Then, water being formed, there is

$$\left.\begin{array}{ll} NO_5 + C_6H_5O & \\ -O_2 \quad -H_2 & \end{array}\right\} = NO_3 + C_6H_3O;$$

the hypo-nitrite of pteleyl being produced.

I did not make any determination of the quantity of nitrogen in this body, as from the explosive way in which the decomposition went on, I did not conceive the result could be one deserving of much confidence.

XIII. OF THE MESITIC ALDEHYD.

I have mentioned that the thinner of the fluids generated by the action of nitric acid on mesitic alcohol, was rendered impure by the presence of a thicker substance, the quantity of which increased according as more red fumes were generated by the boiling of the mixture. This heavy thick fluid is the mesitic aldehyd; which, however, cannot be obtained pure in this way, as a considerable quantity of the hypo-nitrite of pteleyl remains unaltered. By means of the action of nitric acid on mesitylene, it may be obtained quite pure. When nitric acid is boiled with mesitylene, the latter is completely converted into a reddish yellow, thick, and heavy fluid, of a sweetish, but penetrating odour. When it appears no longer altered by fresh quantities of acid, it may be well washed with water, and dried by chloride of calcium.

The composition of this body was determined by the following analyses:

A. 0.385 fluid gave
0.243 water.
0.918 carbonic acid.

B. 0.410 of another quantity gave
0.266 water.
0.943 carbonic acid.

Whence the composition per cent.

	A.	B.	
Carbon =	65.95	63.70	100.00.
Hydrogen =	7.00	7.22	
Oxygen =	27.05	29.08	

The formula $C_6H_4O_2$ gives

$C_6 =$	36.8	64.8
$H_4 =$	4.0	7.0
$O_2 =$	16.0	28.2
	56.8	100.0

The production of this substance, by the action of nitric acid, as well on mesitic alcohol as on mesitylene, is easily understood. Thus

$$\left.\begin{array}{l} C_6H_6O_2 + NO_5 \\ -H_2 \quad -O_2 \end{array}\right\} = C_6H_4O_2 \text{ and } NO_3, \text{ which is expelled ;}$$

and

$$\left.\begin{array}{r} C_6H_4 + NO_5 \\ -NO_3 \end{array}\right\} = C_6H_4O_2.$$

$C_6H_4O_2 = C_6H_3O + HO$; hydrated oxide of pteleyl, or the aldehyd of the mesitic series.

This substance is but sparingly soluble in water; in an alkaline solution it instantly dissolves, giving a yellowish brown liquor. It absorbs dry ammonia with great rapidity, forming a brown, resinous-looking mass, which dissolves in water; and the solution, by cautious evaporation, yields crystals of the mesitic aldehyd ammonia. If a solution of this aldehyd ammonia be added to a neutral solution of nitrate of silver, there is immediately produced a yellow precipitate, which, when heated in the liquor, gradually grows black; the reduction is, however, in this way, imperfect. On the contrary, if the oxide of silver be separated, by a drop of water of potash, it is immediately reduced, the metal being deposited mostly as a black powder, and only partly and occasionally lining the interior of the tube. In no case is the mirror surface generated, which is produced in the reduction of silver by the aldehyd from ordinary alcohol.

There is no doubt but that an acid having the radical pteleyl C_6H_3 as its basis is here produced, by a reaction similar to that which forms acetic acid, in the reduction of silver by vinic aldehyd. I have not, however, attempted to isolate it, or to determine its identity with that resulting from other processes now to be described.

XV. OF THE MESITIC CHLORAL.

The action of chlorine on mesitic alcohol has been examined by Matteuchi and by Liebig; the latter celebrated chemist has described with great accuracy the properties of the heavy oily matter thus formed, and to which I give the name of the Mesitic Chloral. He likewise published an analysis of it, which differs very little from the truth, although he states expressly that he does not bring it forward as correct, but merely as proving that the fluid in question contains chlorine, which Matteuchi had strenuously denied. The action of chlorine on pyroacetic spirit is accompanied by the disengagement of a large quantity of muriatic acid gas; when the action has entirely ceased, the liquor must be boiled to drive off the excess of muriatic acid which remains dissolved, and then dried by digestion on chloride of calcium. It can scarcely be distilled without undergoing alteration, becoming dark-coloured and opaque, while muriatic acid gas is disengaged. It boils at about 260°. Its odour is excessively irritating to the nose and eyes, producing profuse weeping, which lasts for several days; and some of it having accidentally spilled on the hand, produced reddening and vesication as complete as that by cantharides, but much more tedious in healing. On analysis:

A. 0.930 material gave
0.251 water.
0.958 carbonic acid.

B. 0.880 gave
2.028 chloride of silver.

Hence results the composition

$$\left.\begin{array}{ll}\text{Carbon} & = 28.48\\ \text{Hydrogen} & = 3.00\\ \text{Chlorine} & = 56.83\\ \text{Oxygen} & = 11.69\end{array}\right\}\ 100.0.$$

Liebig's analysis gave

$$\left.\begin{array}{ll}\text{Carbon} & = 28.0\\ \text{Hydrogen} & = 2.8\\ \text{Chlorine} & = 52.6\\ \text{Oxygen} & = 16.6\end{array}\right\}\ 100.0.$$

In order to ascertain whether there was formed, by the action of small quantities of a base on this chloral, a body analogous to chloroform, I added to a certain quantity as much potash liquor as dissolved about one-half. The residual heavy fluid, which differed but very little in odour and appearance from its state before the action of the potash, was analyzed.

A. 0.500 material gave
0.164 water.
0.547 carbonic acid.

B. 0.774 material gave
0.841 carbonic acid.
0.241 water.

Whence follows

	A.	B.
Carbon =	30.25	30.04
Hydrogen =	3.64	3.44

As the quantity of carbon, remaining almost absolutely unaltered, proved the fluid analyzed to be unchanged chloral, it was thought unnecessary to determine the chlorine by itself.

The results just obtained may be considered as agreeing tolerably well with each of the following formulæ:

$C_6 H_3 O_2 cl_2$ gives

C_6 =	36.84	29.07
H_3 =	3.00	2.37
O_2 =	16.00	12.65
cl_2 =	70.84	55.91
	126.68	100.00

$C_6 H_4 O_2 cl_2$ gives

C_6 =	36.84	28.86
H_4 =	4.00	3.13
O_2 =	16.00	12.53
cl_2 =	70.84	55.48
	127.68	100.00

The only remarkable difference, between these formulæ, consists in the proportion of hydrogen. It is very unusual, in an analysis of an organic substance, and particularly in that of one containing chlorine, to obtain too small a value for the hydrogen, as in general the error of experiment throws the quantity of hydrogen above the truth. Now here, Liebig, in an analysis, (on which, however, he warns us not to rely,) obtained 2.8; and I obtained in one case 3.0, whilst the theory of the latter formula is 3.13. But it must be recollected that, the first formula assigning 2.37 for the hydrogen, Liebig must have gotten 0.43, and I must have obtained 0.63, 1.27, and 1.07 of hydrogen too much, which is a supposition more improbable than the former.

From the reaction of the chlorine, we may explain the origin of the mesitylic chloral, on either formula; but the decomposition in the case of $C_6 H_3 O_2 Cl_2$ is much more complex. Thus, we must consider the pyroacetic spirit, as really an alcohol, and that but one atom of its hydrogen pre-exists as water; and then, applying the principle of Dumas's theory of substitution, that atom is removed without being replaced, but the further elimination of the hydrogen is accompanied by the substitution of an equivalent quantity of chlorine. Thus

$$\left.\begin{array}{l} C_6 H_5 O + HO \\ - H_2 + Cl_2 - H \end{array}\right\} = C_6 H_3 O_2 Cl_2.$$

Taking the formula $C_6 H_4 O_2 Cl_2$, the reaction becomes much more simple, and consists merely in the elimination of two equivalents of hydrogen, and their replacement by two of chlorine. This formula I am the more strongly disposed to admit, from the action of bases on the mesitic chloral.

When this mesitic chloral is put in contact with a base, there is produced a deep reddish-brown solution, the chloral disappearing completely, if the base be in excess; there is produced a large quantity of a metallic chloride, and a salt of the base employed with a new acid, the nature of which may be deduced from the circumstances of the reaction by which it is formed. The chlorine abandoning the other constituents of the mesitic chloral in order to unite with the metal whose oxide has been employed, it must be replaced by an equivalent quantity of oxygen, and the body $C_6 H_4 O_4 = C_6 H_3 O_3 + HO$ must be produced. Such may be expected to be the composition of the acid in the new salt produced; and until its nature and composition are more accurately examined by other chemists, it may receive the provisional name of *Pteleic Acid.* The salts which it forms are almost all soluble; those with the alkalies and alkaline earths are in solution coloured brown, but do not possess any of the reducing properties of the similar compounds of mesitic aldehyd.

In presenting this memoir to the Royal Irish Academy, I noticed the existence of two acids formed by the action of acetone on permanganate of potash. A salt is at first obtained quite neutral, which after a little time breaks up into a carbonate, and a salt of another acid. The investigation of the properties and composition of these, as well as the more minute examination of the compounds of the pteleic acid, will form the subject of another paper.*

---

* The principal Memoirs on Pyroacetic Spirit by previous authors are the following:—

Derosne; Annales de Chimie, vol. lxiii. p. 267.—Chenevix; Annales de Chimie, vol. lxix. p. 5. —Macaire and Marcet; Bibliotheque Universelle, vol. xxiv. p. 126.—Matteuchi; Annales de Chimie et de Physique, vol. xlvi. p. 429.—Liebig; Annalen der Pharmacie, vol. i. p. 225.—Dumas; Annales de Chimie et de Physique, vol. xlix. p. 208.